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13. ABSTRACT (Maximum 200 words) A range of monoepony additives for epoxy resins, and non-reactive additives for polyimides, have been examined with a view to understanding the mechanism of their fortifying" action, and to examine their usefulness in adhesive applications. An increase in strength of 50% and an increase in modulus of 40% is achievable by this method, along with a decrease in water uptake, decreased expansion coefficient, and a modified failure mechanism. These properties of the bulk resin translate into modest improvements in adhesive bond performance, particularly for low temperature cured systems, and in humid environments. It should be cautioned, however, that the effect of the additives will vary with the geometry of the joint and the test procedure. The mechanism of property modification is explained on a quantitative basis using the concept of free volume. The contributions of molecular interactions and of the depression in glass transition temperature are separated. The monoepony additives are shown to function more efficiently than unreactive additives in epoxy systems. A synergism between these additives and CTBM rubber modifiers is also reported					
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MODIFIED EPOXY ADHESIVES AND PRIMERS

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Andrew Garton
Professor of Chemistry
Institute of Materials Science, Box U-136
University of Connecticut
Storrs, CT 06269-3136
Tel 203 486 4188
Fax 203 486 4745

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A. Statement of Problem

A.1. Historical Background

"Epoxy Fortifiers" were invented and patented at the National Research Council of Canada by a group headed by Mr. Paul McLean. A range of materials was manufactured and marketed by Uniroyal Chemicals, who were taken over by Polysar, who were then taken over by Nova Corp. The purpose of this ARO project was to explore the scientific basis of the phenomenon (an increase in stiffness and strength along with a change in fracture properties), and to explore the potential of these materials in adhesive applications.

A Technical Report (dated Jan 26, 1989) was issued to ARO by this author, describing the performance of model systems (VCDHAA and EPPHAA) which resembled, but did not duplicate, the commercial materials. It was concluded that some adhesive bonding properties of epoxy systems could be

improved significantly by the incorporation of 5-15% of these additives, particularly for low temperature cure applications. The molecular basis of the phenomenon was rationalized on a semi-quantitative basis in terms of "antiplasticization" - a reduction in free volume, and hence molecular mobility, brought about by interactions between a stiff polar additive and a polar glassy matrix. The occurrence of extensive yielding before failure in a tensile test ("ductility", see later for more comments on this term) was attributed to the anomalously low Poisson's Ratio of the modified polymer, which resulted in an anomalously high increase in free volume as the material was strained. At high strains, the strain-induced free volume exceeded that required for long range segmental mobility and yielding occurred. A reasonable summary of these early findings is available in reference 1, and references cited therein.

A.2. Recent Developments in the Literature

Research has continued in the U.S. and abroad into the phenomenon of antiplasticization, and the related subject of the influence of free volume on polymer properties. Techniques such as NMR spectroscopy, positron annihilation, and fluorescent molecular probes have been used in these investigations. The qualitative picture of the phenomenon, i.e. the hindering of short range macromolecular motions, has remained unchanged but more information is now available about the detailed nature of these motions. Two particularly noteworthy advances in the quantification of the phenomenon are described below.

Paul and Maeda (2) have shown that a simple definition of free volume correlates well with the mechanical and transport properties of antiplasticized thermoplastic polymers.

$$V_F = V - V_0 = [(V - V_0)_d w + (V - V_0)_p (1 - w)] + V_e \quad (1)$$

where V_F is the specific free volume of the mixture, which is the difference between the measured specific volume V and the specific occupied volume V_0 . V_0 is the van der Waals occupied volume calculated from tabulated atomic volumes. The term w is the weight fraction of additive (diluent) and the subscripts d and p refer to the diluent and polymer respectively. The term V_e is the excess volume of mixing, i.e. the amount by which the specific volume of the mixture differs from the weighted sum of the specific volumes of the polymer and diluent. This model does not examine quantitatively the factors which are responsible for the magnitude of V_e , but the authors conclude that the thermal history and the magnitude of the molecular interaction between additive and diluent are important.

Vrentas et al (3) use a more complex model to account for free volume changes. Free volume is calculated from diffusion measurements, rather than the van der Waals volume of the previous model. In earlier work, the

authors developed the concept of an interstitial volume, which must be added to the van der Waals volume in calculating the free volume. This interstitial volume, although unoccupied, is inaccessible to the additive. A further feature of the model is that an algebraic relation is obtained relating the excess volume of mixing to the depression of glass transition temperature of the polymer by the additive. While this model has a more quantifiable basis, it arrives at a similar ranking of effectiveness of antiplasticizing additives as the simpler, earlier, model. A correspondence between the two sets of authors continued in the literature.

The above models are of limited applicability to the epoxy systems described in this report since chemical reaction occurs between the additive (monoepony compounds) and the polymer matrix (epoxy/amine), and so there will be an additional volume change associated with the chemical reaction. The term "internal antiplasticization" has been used to describe the modulus changes in non-stoichiometric epoxy systems (4,5,6). That term will be used here to distinguish the reactive additive case from the addition of an unreactive additive (external antiplasticization). In the case of non-stoichiometric epoxy/amine systems, increases in modulus are rationalized in terms of the "packing density" of the network - the presence of loose ends in the non-stoichiometric network allows more efficient packing of the molecules, and hence a reduction in free volume. Contrary to intuition, a very highly crosslinked system can have higher free volume than a less crosslinked system, because the presence of chemical crosslinks can hinder the development of non-covalent bonding interactions between polymer chains.

Finally, one particularly notable development refers specifically to polyimides. Workers at the NASA Langley Research Center (7) explored the use of diimides and diamic acids as viscosity modifiers in melt-processable polyimides. They successfully lowered the melt viscosity of LARC-TPI, leading to improved composite properties, and found that the bulk polymer exhibited lower water uptake, increased modulus, decreased dielectric constant, and decreased free volume. Positron annihilation was used to measure free volume. The paper by St.Clair et al (7) is the only example of antiplasticization of polyimides, other than from this project, in the open literature.

The model developed here (section B.6) will include some aspects of all of the above, and will demonstrate that the behavior of "fortifiers" can be explained on a quantitative basis using the concepts of free volume and antiplasticization.

A.3 Statement of Problem and Approach

Materials described as "Epoxy Fortifiers" have generated considerable interest, but have been the subject of many confusing and contradictory statements, both positive and negative. The purpose of this project has

been to develop a quantitative mechanism to explain and predict performance, and to examine the effectiveness of these materials in a range of adhesive applications.

The approach to the problem has been to examine two very different systems (based in part on the different Ph.D. thesis topics of the two students involved, Ed Shockey and Gautam Haldankar). In the first part, the behavior of monoepoxy additives in epoxy/amine systems is examined, as an example of internal antiplasticization, while the second part describes non-reactive additives in linear polyimides, as an example of external antiplasticization.

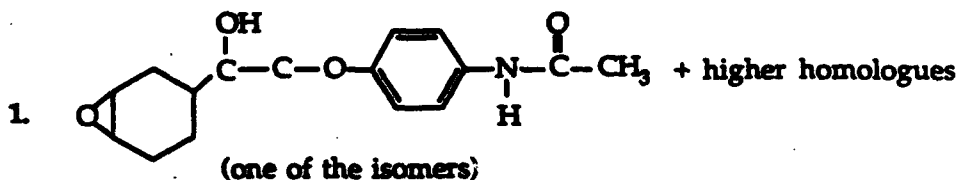
B. Summary of Most Important Results

B.1. Description of Systems Studied

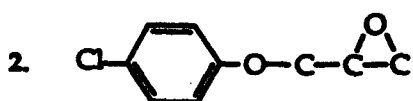
The epoxy resin system was the well-established and widely-studied Epon 828 (Shell), cured with methylene dianiline (MDA). Epon 828 consists largely of the diglycidyl ether of bisphenol-A (DGEBA), but with some oligomers present. Mixing followed conventional procedures, and a 1:1 epoxy:amine stoichiometry was followed in all experiments. Unless stated otherwise. This necessitated increasing the MDA level in the presence of monoepoxy additives. The cure history was one hour at 120°C followed by two hours at 150°C. The rubber modified epoxy was also based on Epon 828, but with 15 phr (parts per hundred of resin) of carboxy-terminated nitrile rubber (Hycar 1300X8, B.F. Goodrich) pre-reacted into the resin according to the manufacturers specifications.

Five monoepoxy additives were examined at concentrations up to 30 phr. The structures are shown in Figure 1. Structures II-V were obtained commercially as reagent grade materials. VCDHAA was prepared as described by Garton et al (8), and was a complex chemical mixture. The major component was a monoepoxy adduct formed by reaction of the phenolic OH of HAA (4-hydroxyacetanilide) with vinyl cyclohexene dioxide, with some oligomers. The starting materials were largely removed by washing and reprecipitation. The average molecular weight of the purified VCDHAA was 373 g/mol, with an epoxy equivalent of 396 g/equiv. NMR spectroscopy showed that the two epoxy groups of VCD had reacted to an almost equal extent. Liquid chromatography showed that the 1:1 adduct consisted of a large number of isomers and enantiomers (9), as might be expected from the number of chiral centers in the VCD molecule, and its four potential sites for nucleophilic attack. The additives were dissolved in the epoxy resins, usually at less than 80°C, and mixed with the curing agent in the conventional fashion. Because some additives accelerated the cure, it was necessary to pour the specimens (3mm thick sheets) immediately after degassing.

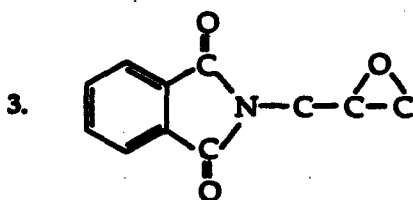
Specimens for dynamic mechanical analysis were milled as 0.65x3.2x35 mm strips, and examined on a Polymer Laboratories DMTA in the tension mode. Tensile strength and modulus were determined according to ASTM D638 (type II), using an Instron model 1011. The dog-bone specimens were machined by Paul McLean of the National Research Council of Canada. Volume dilation during the tensile test was measured using perpendicular, glue-on, strain gages (Measurement Group, Inc.). Fracture energies were measured using compact tension specimens as described by Ting and Cottingham (10). Glass transition temperature (T_g), solvent extraction, coefficient of thermal expansion (CTE), shear strength, density, and water uptake measurements were performed in a conventional fashion (9).



VCDHAA



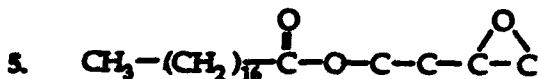
1,2-epoxy-3-(p-chlorophenoxy) propane (ECPP)



N-(2,3-epoxypropyl) phthalimide (EPI)



2,3-epoxypropyl-p-methoxyphenyl ether (EPMPE)

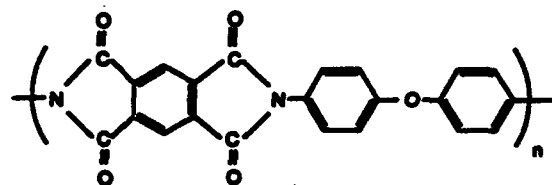


Epoxybutyl Stearate (EBS)

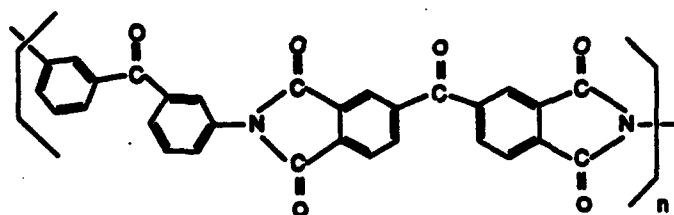
Figure 1 Monoepoxy additives for epoxy resins

Several geometries of adhesive joints were tested. A torsional napkin ring joint test, as developed by Lin and Bell (11), was used to provide a relatively uniform stress field. The joints were constructed from 1018 mild steel, and were citric acid treated (9,11). Single lap-shear joints were made using degreased 1038 carbon steel, so as to provide a more complex stress field more typical of adhesive applications. Both types of adhesive joint were also subjected to a range of humid aging environments (90% humidity and 67°C or water at 67°C for lap shear joints, water at 57°C for napkin ring joints).

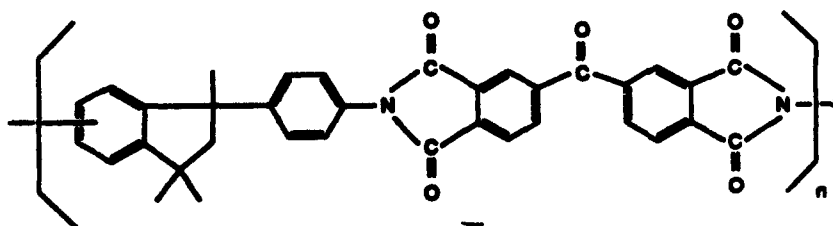
The epoxy experience was extended to three linear polyimides (Fig.2). The PI-2540 (DuPont) and Durimid 100 (Rogers) were obtained as amic acid solutions, which were thermally imidized as thin films. The Matrimid polymer was fully imidized, but because of its relatively flexible backbone it could be dissolved in a range of common solvents. The form of the specimens was usually as thin films cast on release-agent treated glass. Full details of fabrication histories are provided elsewhere (12)



PI-2540 (DuPont)



Durimid 100 (Rogers)



Matrimid 5218 (Ciba-Geigy)

Fig.2 Polyimide structures

The analytical and characterization procedures resembled those used for the epoxy system. However, much more extensive use was made of liquid chromatographic (LC) analysis, since we demonstrated that these additives were unreactive with the polyimide, and so could be extracted for analysis. The range of additives for polyimides is shown in Figure 3. EPPHAA was chosen for initial study because it was effective for epoxy systems, and could be prepared in a relatively pure state (13). However, we realized it would have relatively poor thermal stability at typical polyimide fabrication and service temperatures and so we also examined a series of substituted fluorenes. This allowed us to make systematic changes in additive structure. While these materials were thermally stable at the cure temperature, some members of the series were significantly volatile under the conditions of curing the thin films at temperatures up to 300°C

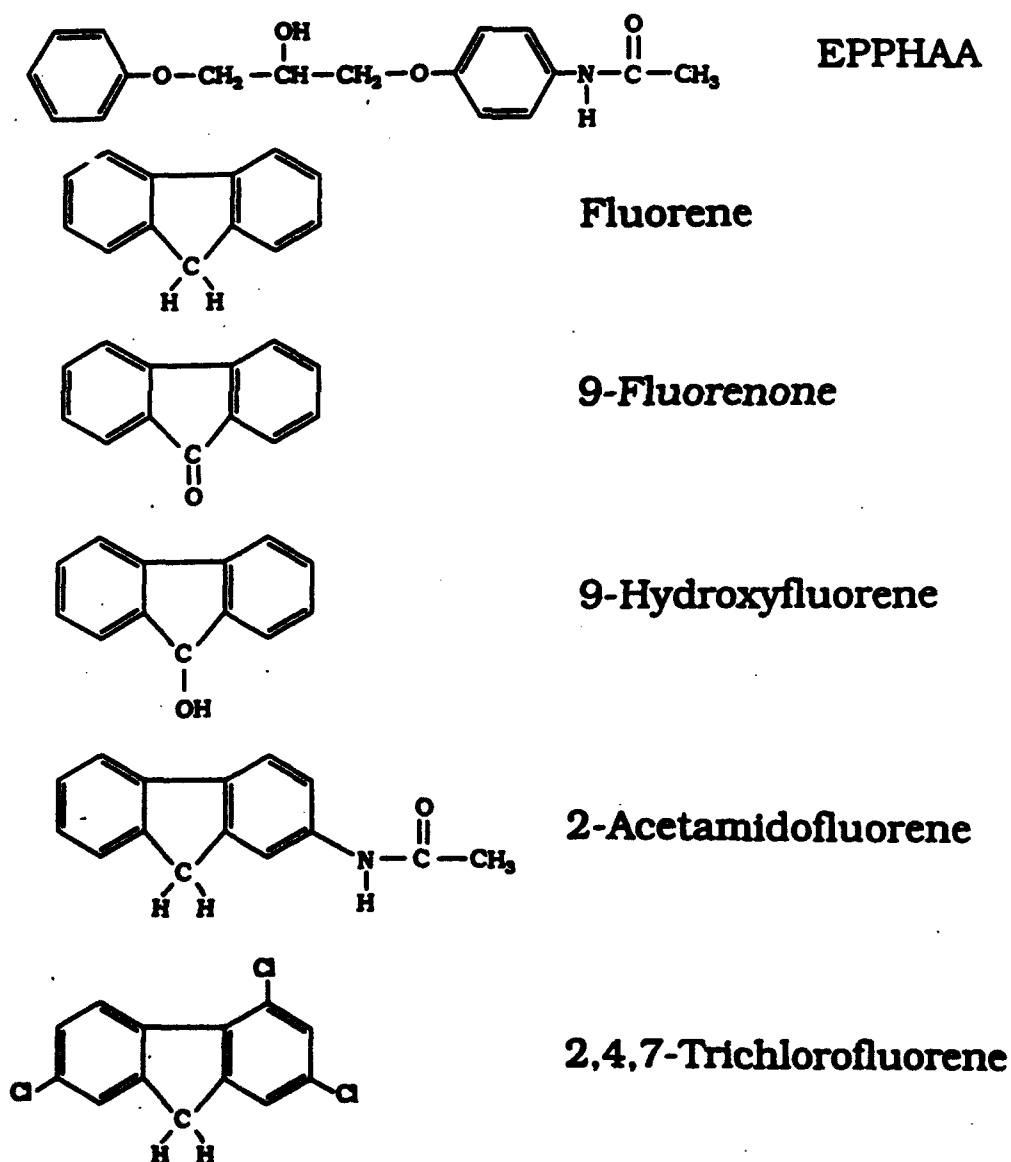


Figure 3 Additives for the polyimide systems

B.2 Bulk Properties of Epoxy Systems

With the exception of the additive EBS, all cured specimens prepared without rubber modifier appeared to be single phase materials (optically clear, single T_g). The most striking modification to the bulk properties of the epoxy systems is in the tensile test data (Fig.4). In the example shown, the strength was increased 50%, and the modulus about 40%, by the addition of 19% (30 phr) VCDHAA.

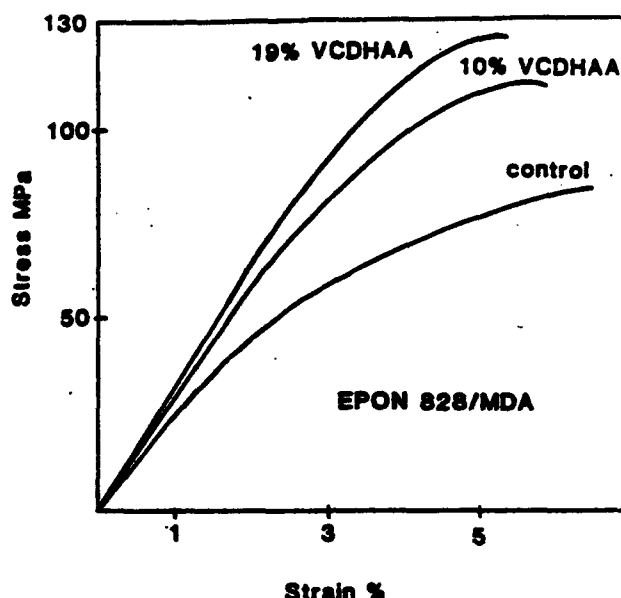


Fig.4 Tensile stress:strain curves for cured epoxy resin, with and without the additive VCDHAA

The effect on the modulus was confirmed by DMA, as we have described elsewhere (8). At low temperatures (e.g. -100°C), the modulus is little affected by the additive, while at high temperatures (e.g. $>150^{\circ}\text{C}$), the modulus is reduced below that of the control, because of the reduction in T_g . However, for a wide range of temperatures and frequencies, the storage modulus of the modified epoxy specimen is appreciably higher than that of the control. DMA also provides information about the viscoelastic nature of the polymer, through the loss modulus and tan delta. These data are summarized in Table 1. The consistent trend is that the additives reduce the glass transition temperature by up to 30°C . There is also a reduction in the Beta relaxation temperature, but, more importantly, the area under the beta relaxation is reduced significantly. The beta relaxation corresponds to short range motions of the epoxy network, and these motions are being suppressed with the additive present, consistent with the effect on the room temperature modulus. The activation energy for the beta relaxation (determined by variable frequency measurements) was consistently lower for the additive containing specimens than for the control. The molecular basis for these phenomena is discussed in section B.6

Table 1 DMA analysis at 1 Hz

Sample	T _g (°C)	β-transition temperature (°C)	Normalized area under tanδ	E' (Pa) at 25°C
Control	174.0	-60	100	2.43E+09
+10 VCDHAA	156.5	-67	80	2.83E+09
+20 VCDHAA	141.5	-69	59	3.19E+09
+10 EPI	159.5	-59	86	2.67E+09
+20 EPI	152.5	-66	80	2.87E+09
+10 ECPP	159.0	-64	92	2.63E+09
+10 EPMPE	159.0	-64	93	2.62E+09

The tensile test can also be used to illustrate that considerable volume dilation occurs upon straining. Figure 5 shows that the volume increase of the VCDHAA containing specimen is significantly higher than that of the control. We believe that this is the cause of the yielding observed in the tensile test (Fig.1), as will be discussed further in section B.6

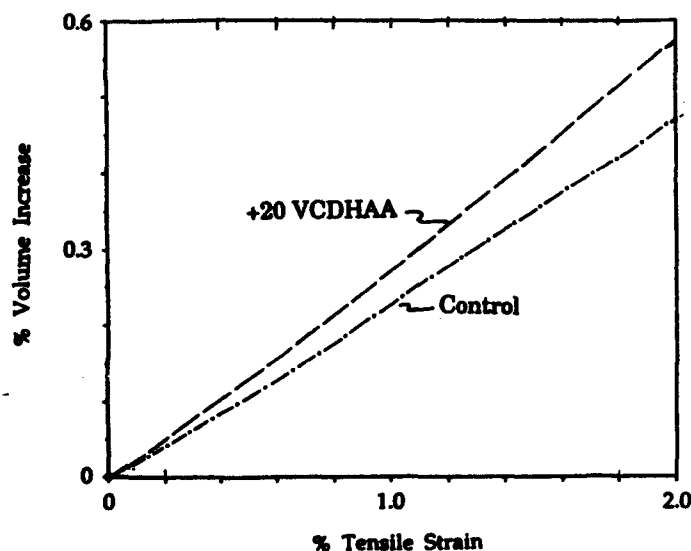


Fig.5 Increase in volume under tensile strain
 --- control -.- 20 phr VCDHAA

We stress here that the yielding observed in the tensile test does not imply that these materials are "tough". Figure 6 shows that, for the chosen test conditions, the fracture energy is reduced by the addition of VCDHAA. If the data were expressed in terms of critical stress

concentration (K_{Ic}), the data would be more comparable, because of the inclusion of a modulus term. We have also demonstrated elsewhere that the fracture process in materials such as these is highly strain rate dependent, and also depends on the thermal history of the specimen (13). In order to achieve "toughness", it is necessary to incorporate rubber additives (section B.3).

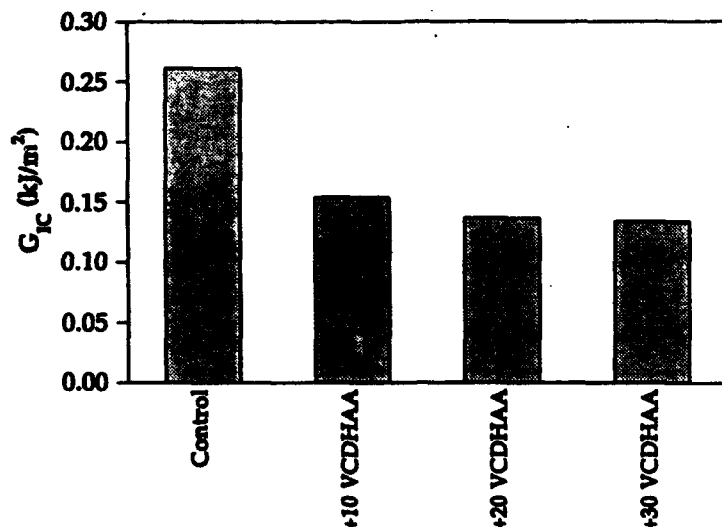


Fig.6 Fracture energy of VCDHAA-modified epoxy system

An examination of the temperature dependence of tensile properties is particularly informative concerning the mechanism of property modification. Figs 7 and 8 show that as the temperature increases, additive VCDHAA changes from being an antiplasticizer to being a plasticizer, i.e. an increase in modulus and decrease in strain to break changes into a decrease in modulus and an increase in strain to break. This is discussed further in section B.6

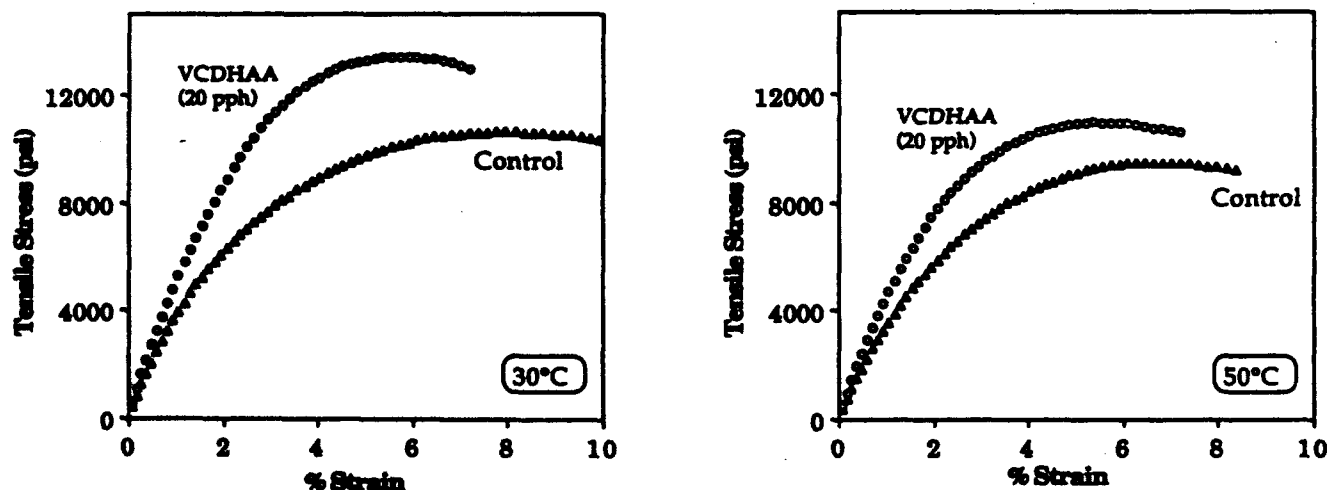
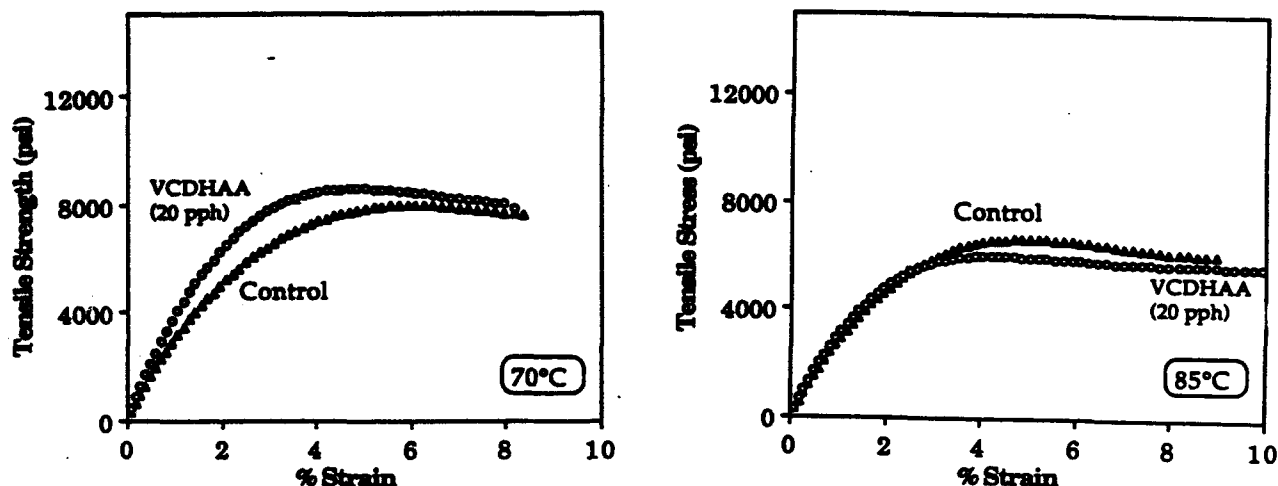


Fig.7 Tensile curves at 30°C and 50°C

Fig.8 Tensile curves at 70°C and 85°C



Other physical and mechanical properties of interest include :

1. A reduction in glassy CTE of up to 25% - this could be important if high cure temperatures are used, since internal stresses would be reduced.
2. A reduction in water uptake - even though some of these additives are polar materials, the rate of water uptake in humid environments was decreased significantly. This effect diminished as the temperature was raised, while at long times and elevated temperatures (e.g 50°C, 95% humidity, 400 hours) the water uptake curves cross, indicating the the additives may reduce the kinetics of water uptake but the equilibrium water solubility may be higher
3. The density of the additive-containing specimens is appreciably higher than one would calculate from a rule of mixture approach. While some of this is due to chemical reaction, we also believe that there is a significantly negative volume of mixing in these systems.
4. The additive VCDHAA does not react fully with the crosslinked polymer and may be partially extracted with a solvent. Additive EPI reacts fully. This is reflected in their effect on the T_g (Table 1), and the relative magnitude of the contributions to the modulus increase (section B.6)

B.3 Rubber Modified Epoxy Systems

As described earlier, CTBN rubber additives are used to increase the toughness of epoxy systems. We explore here the consequence of simultaneous addition of rubber and antiplasticizing additives.

Figure 9 summarizes the effect of rubber additives alone, and in combination with VCDHAA. When used alone, the rubber additive increases the fracture energy, as expected, but decreases the modulus and shear strength. When used in combination with 20 phr VCDHAA, the modulus and

shear strength are returned close to the control values, and, surprisingly, the fracture energy is increased still further. The only negative consequence is a further decrease in T_g . We therefore conclude that VCDHAA and CTBN rubbers can exhibit a synergistic effect on the properties of amine-cured epoxies.

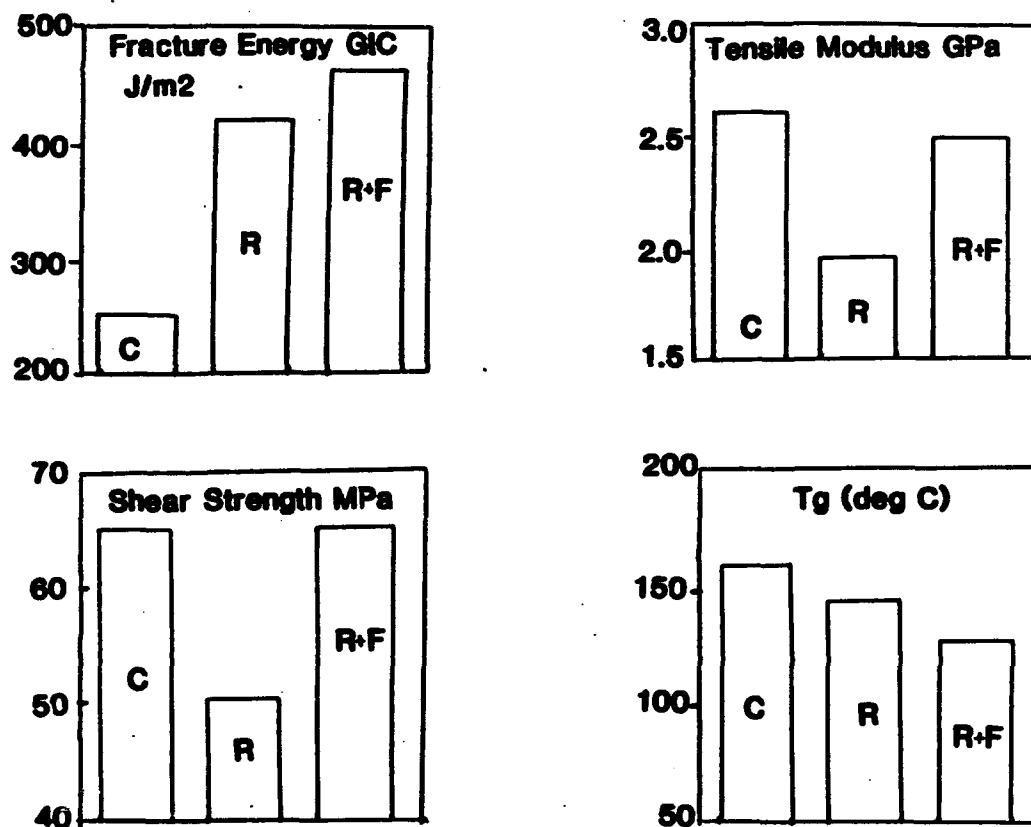
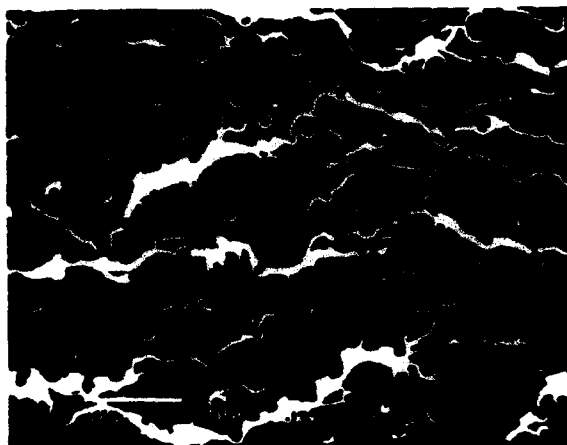


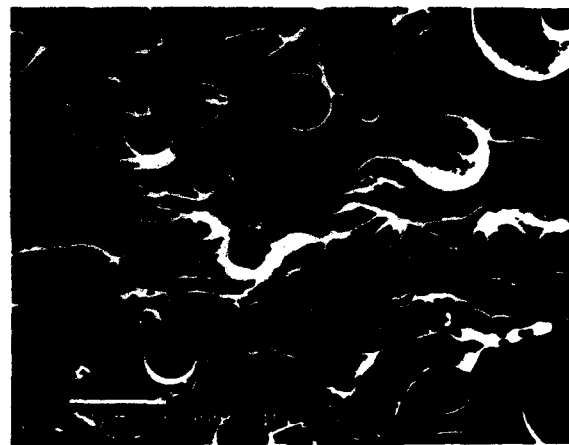
Fig.9 Effect of addition of 15phr CTBN rubber toughener alone (R) and in combination with 20 phr VCDHAA (R+F)

We attribute this synergism to a combination of antiplasticization of the epoxy continuous phase and modification of the particle size distribution of the dispersed rubber phase. Figure 10 shows that when CTBN alone is added, the dispersed phase has a relatively uniform particle size. With CTBN and VCDHAA, there is a broad distribution of phase sizes, ranging from <1 micron to >10 microns. Our increase in fracture energy is therefore consistent with the observation of Kinloch (14) that for a fixed volume of the dispersed phase, a bimodal distribution of phase sizes gave a higher fracture energy than a unimodal distribution. The T_g of the CTBN + VCDHAA modified epoxy, is similar to that of the system modified by VCDHAA alone, implying that phase separation of the rubber was essentially complete. The mechanism by which the morphology is changed could involve both a change in the solubility parameter of the uncured epoxy, and also a change in the polymerization kinetics, which will modify the manner in which the initially-soluble CTBN phase separates from the curing polymer.

**Fig.10 Electron micrographs of fracture surfaces of (a) epoxy + 15phr CTBN
(b) epoxy + 15phr CTBN + 20phr VCDHAA**



(a)



(b)

Other related property changes associated with the addition of VCDHAA to a rubber-modified epoxy are a suppression of the beta relaxation, an increase in density, and a decrease in water uptake, as expected from the antiplasticization of the continuous phase (9).

B.4. Adhesive Properties of Epoxy Systems

Table 2 shows that the increase in shear strength of the epoxy system translates directly into increased strength of the torsional napkin ring adhesive joints, both for VCDHAA and VCDHAA and CTBN toughener. This is a relatively simple joint geometry, where fracture occurs close to, but not at, the interface.

Table 2 Comparison of shear strength of polymer and of adhesive joint

Sample	Torsional Shear Stress τ_{max} (MPa)	Normalized Shear Stress τ_{max}	Shear Strength of Bulk Resin (MPa)
Control	66.52 \pm 3.1	100	67.84 \pm 2.3
+20 VCDHAA	79.59 \pm 2.8	120	78.18 \pm 2.6
+15 CTBN	51.81 \pm 3.8	78	53.88 \pm 2.4
+15 CTBN +20 VCDHAA	63.13 \pm 1.0	95	68.66 \pm 0.8

The performance of the adhesive bonds in water also reflects the decreased water uptake of the bulk epoxy (Section B.2). Figure 11 shows that torsional shear joints made with epoxy + VCDHAA retain their improved

properties for the first 80 hours immersion in water at 57°C, but the data then cross, consistent with the reduced rate of water uptake, but higher equilibrium water content, in the presence of VCDHAA.

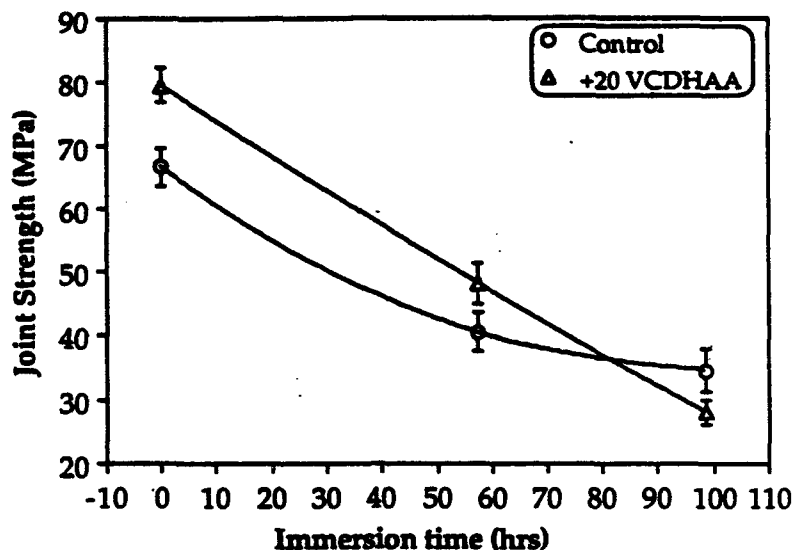


Fig.11 Torsional joint strength on immersion in water at 57°C

Lap shear joints have a much more complex stress distribution than the torsional shear joints. Tension, compression, and peel occur at different positions in the joint. There is a modest increase in strength on incorporation of VCDHAA, but the strength is influenced more by the pretreatment of the steel. Upon exposure to water, the strength decreases, as expected. Again, the VCDHAA containing specimens initially show the greater strength retention, but the data cross after about 20 days at 67°C. Exposure to high humidity, rather than liquid water, highlights the benefits of VCDHAA addition. Figure 12 shows that the fractional improvement in properties (VCDHAA vs control) increases with exposure time, presumably because of the reduced rate of water ingress.

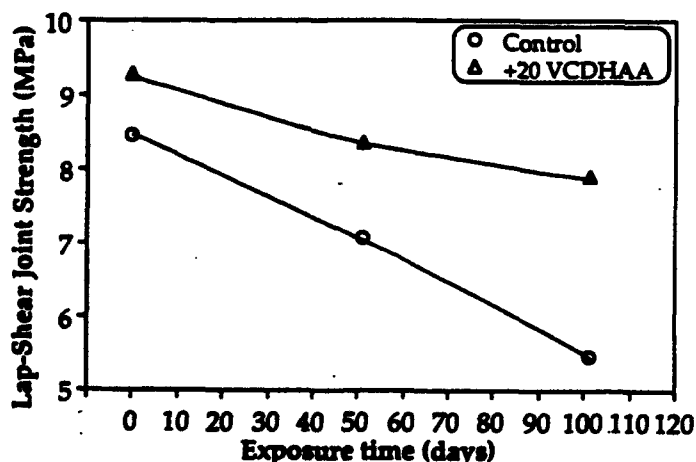


Fig.12 Lap shear joint strength as a function of time of exposure to 90% humidity and 67°C

Adhesive joints can also be modified by the use of antiplasticizing additive as a primer, i.e. localizing its effect in the interphase. As a semi-quantitative demonstration of this phenomenon, we coated the torsional shear joints with a solution of VCDHAA in acetone. Interpenetration of the VCDHAA and the epoxy adhesive then produces a modulus gradient in the interphase. A maximum increase in joint strength of about 25% was achieved by this method (Fig.13). When the VCDHAA primer coating was too thick, it functioned as a weak boundary layer, and the strength was reduced.

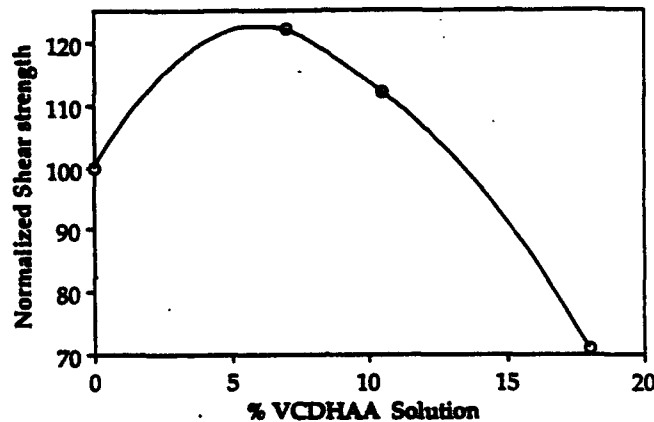


Fig.13 Normalized shear strength as a function of the concentration of the primer solution (hence, indirectly, the primer thickness)

A similar experiment was carried out in a more controlled fashion in collaboration with Dr.K.Reifsnider of Virginia Tech. A glass rod embedded in an epoxy matrix. The rod was coated with successive layers of epoxy/EPPHAA with the concentration of antiplasticizing additive adjusted to give the modulus gradient shown in Figure 14. Jayaraman et al (15) have shown, using the Mori-Tanaka-Benveniste approach, how a property gradient in the interphase affects the stress fields in continuous fiber composites. Their analysis of the properties of the embedded glass rod are continuing.

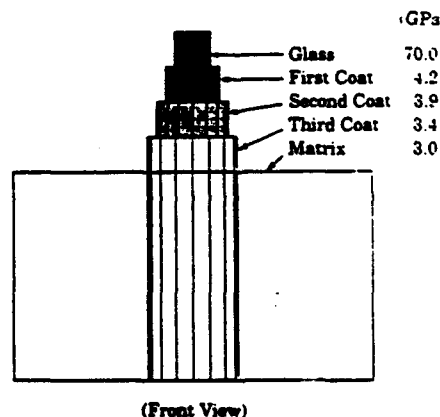


Fig.14 Step-down modulus gradient produced by coatings containing different concentrations of EPPHAA

By these and other related experiments (9), we conclude that antiplasticizing additives can produce modulus gradients at in interphases, and that such graded interphases can be beneficial to adhesive bond and composite performance. As elsewhere in this report, we stress that additives such as those we describe here, when used without CTBN, do not make the epoxy system inherently "tough". Instead, there is an increase in modulus and, in some cases, strength, together with a change in the mode of failure. The effect on complex structures such as adhesive bonds will not always be simple to predict, and the effect on properties will depend on the nature of the test.

B.5 Bulk Properties of Polyimide Systems

Figure 15 shows that the tensile properties the Matrimid 5218 linear polyimide are affected by antiplasticizing additives in a manner similar to that shown for the epoxy systems (Fig.3). Similar data were obtained for the other polyimides (12). However, we stress that linear polyimides such as these are inherently higher-strain materials than the crosslinked epoxies, and the reduction in strain-to-break shown in Fig.15 and elsewhere weighs against the practical use of these additives for the strengthening of unsupported film specimens.

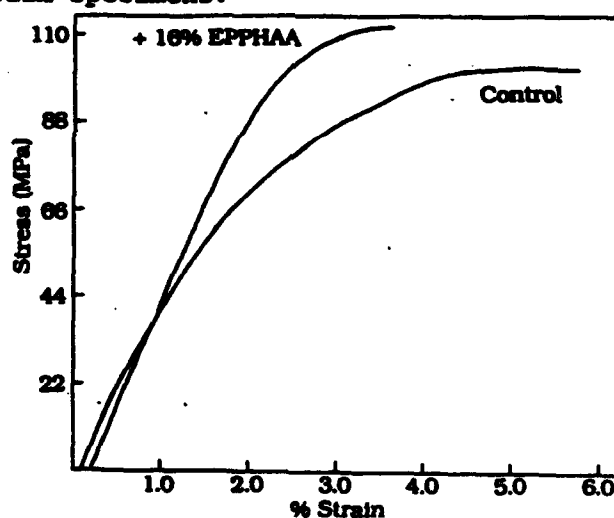


Fig.15 Tensile properties of thin films of Matrimid 5218 polyimide, with and without the additive EPPHAA. Note that the EPPHAA concentration is nominal only, since some was lost by volatilization during film manufacture (see later)

The antiplasticization phenomenon is demonstrated more clearly in the effect on the loss tangent, as measured by DMA. All the chosen additives had the effect, as illustrated in Figure 16, of suppressing the low temperature (ca. -80°C) relaxation, enhancing the ca. 100°C relaxation, and reducing the T_g to varying extents. Figure 17 shows that a 30% increase in room temperature modulus is attainable by this method, and that the enhancement of the intermediate temperature relaxation (ca. 80°C in the Matrimid polyimide) leads to a crossing of the modulus data at elevated

temperatures. With the other polyimides, there was also a crossing of the modulus curves (12), but at a higher temperature than that shown in Figure 17. Unlike the epoxy case, the modulus data do not coincide at low temperatures.

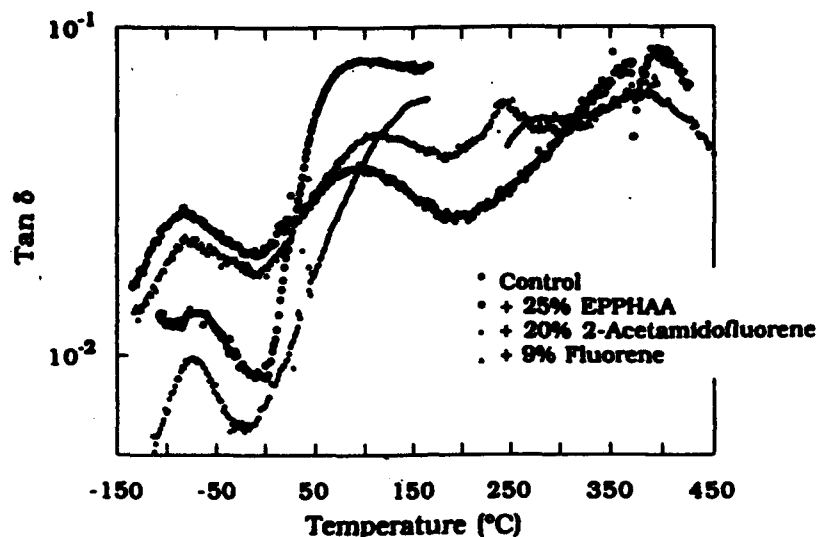


Fig.16 The effect of selected additives on the mechanical loss properties of polyimide PI-2540

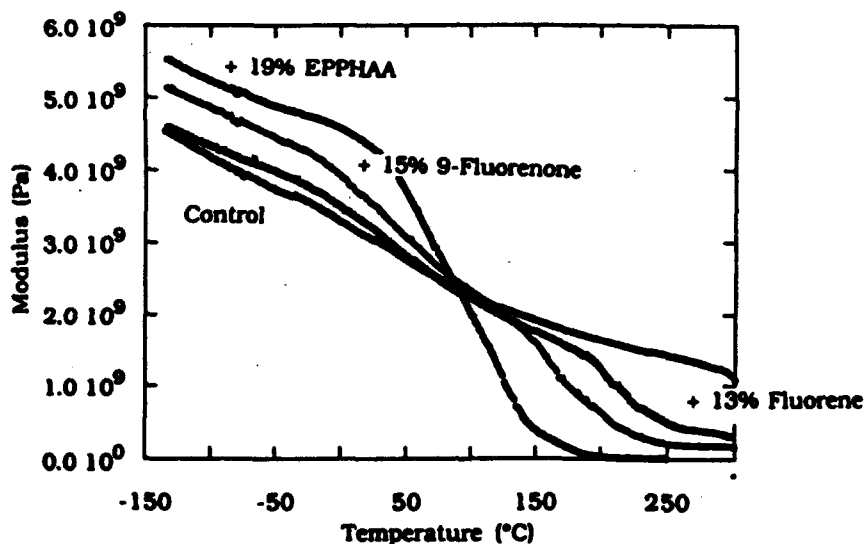


Fig.17 The temperature dependence of the tensile modulus of polyimide Matrimid 5218, with and without additives

The non-crosslinked nature of these systems allows a more complete analysis of the additive function. Films made from the polyimide Durimid 100 were soluble in *m*-cresol at 130°C, even after elevated temperature cure. It was therefore possible to determine whether the additives had reacted during the imidization, or had affected the molecular weight of the polyimide. Figure 18 shows the size exclusion chromatogram (SEC) of the Durimid 100, with and without the additive EPPHAA. Data are presented as elution time only, since the Mark-Houwink constants of the polyimide were

not available. The molecular weight distribution of the polyimide was unaffected by the incorporation of EPPHAA, and the additive also appeared to be unchanged. - This system may therefore be considered as an example of "external antiplasticization" rather than the "internal antiplasticization" of the epoxy resin/monoepoxy additive case. The PI-2540 polyimide was insoluble and so this experiment could not be performed. The Matrimid 5218 polyimide did not require elevated temperature cure, and was initially in a fully imidized state, and so, as expected, was entirely unaffected chemically by the additives (12)

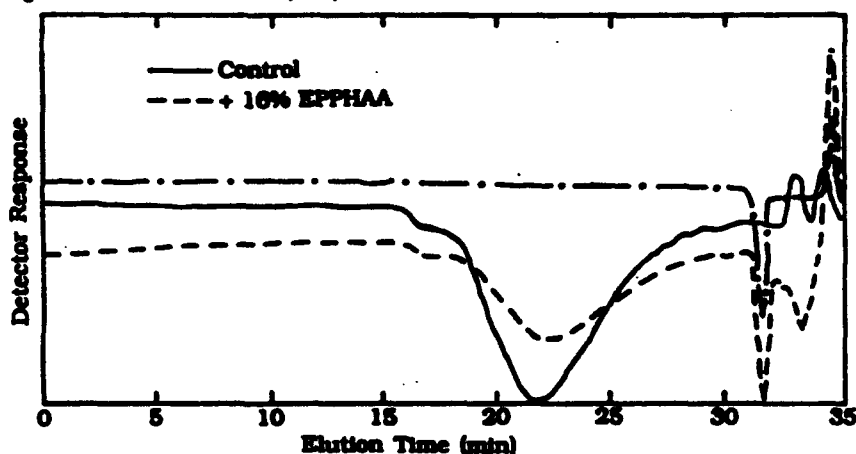


Fig.18 SEC analysis of Durimid 100, with and without EPPHAA. Note the coincidence of the polymer elution data, and the presence of a distinct EPPHAA fraction

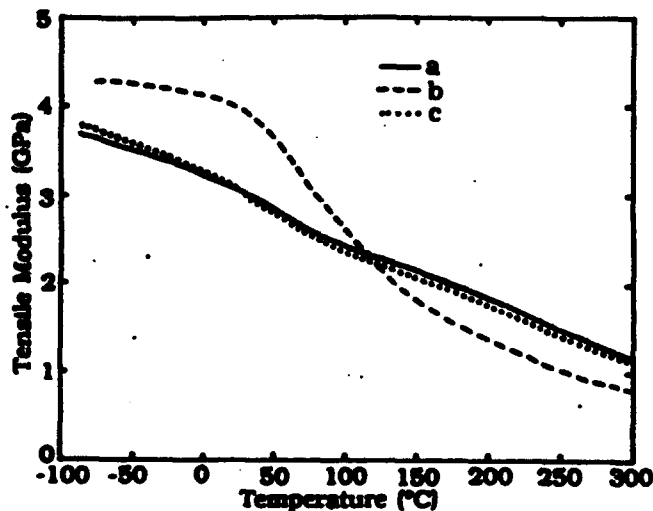


Fig.19 DMA of PI-2540 (a) control (b) + 20phr EPPHAA (c) specimen b after extraction with methylisobutylketone

The chemically unreactive nature of these systems allows an elegant demonstration of the antiplasticization phenomenon. The PI-2540/EPPHAA system was extracted with MIBK - a good solvent for the EPPHAA but a poor solvent for the polyimide. The dynamic mechanical properties were measured before and after extraction. Figure 19 shows that solvent extraction of the EPPHAA returns the properties of the system close to those of the

control, as would be expected if the mechanism of action of the additive was simply antiplasticization.

Solvent extraction and liquid chromatography also provided the means for quantifying the amount of additive present in the films. All the additives are to some degree volatile when exposed to the 300°C temperature necessary to complete imidization, particularly when the specimen is in the form of a thin film. Additive EPPHAA will also be thermally unstable at 300°C because of the presence of the sequence of methylene units. The additive concentrations used in the model development (Section B.6) are therefore determined, post-fabrication, by liquid chromatography.

The property of greatest practical interest for the modified polyimides is water uptake. Polyimides have a physical affinity for water, and are also prone to hydrolysis, and so a reduction in water uptake is relevant to many composite and adhesive applications, as well as to the use of polyimides in electronic components. Figure 20 shows that, for polyimide PI-2540, the water uptake can be reduced considerably by the incorporation of antiplasticizing additives, as would be expected from the decrease in free volume. The 1-2 mil thick polyimide films were exposed to 51°C and 95% relative humidity and the water uptake was determined gravimetrically. Similar reductions in water uptake were also observed for the other polyimides (12)

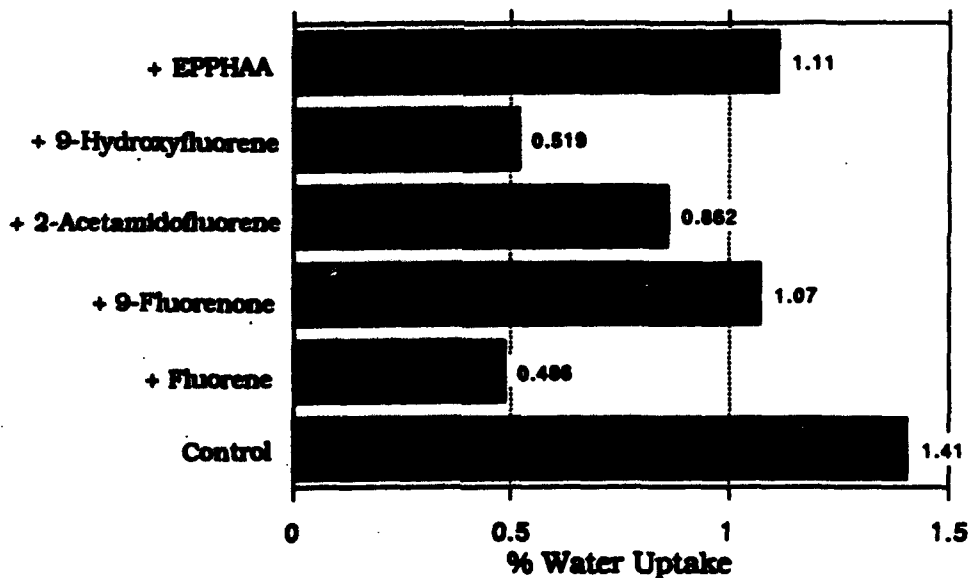


Fig.20 Water uptake by PI-2540

B.6 Mechanistic Basis for Above Behavior (Epoxy and Polyimide)

Our hypothesis was that the behavior of these additives could be explained on the basis of antiplasticization, caused by a reduction in free volume in the presence of the additive. The concept of free volume is that a certain proportion of the volume of the specimen is not occupied by the molecules, and is accessible for motion of the polymer segments, and is one

of the most widely used concepts in polymer science. The manner of calculation of this free volume is the subject of wide debate. We will use a very simple model of free volume, and show that it is adequate to explain our data on a quantitative basis. More sophisticated models of free volume may be more precise, but offer no advantages to this problem. We will divide the volume of the specimen (V) into an occupied volume (V_0) and a free volume (V_f). We will assume that V_0 is temperature independent (this is obviously unrealistic, but this simple model works surprisingly well, and so is the one we chose to use). This is illustrated schematically in Figure 21.

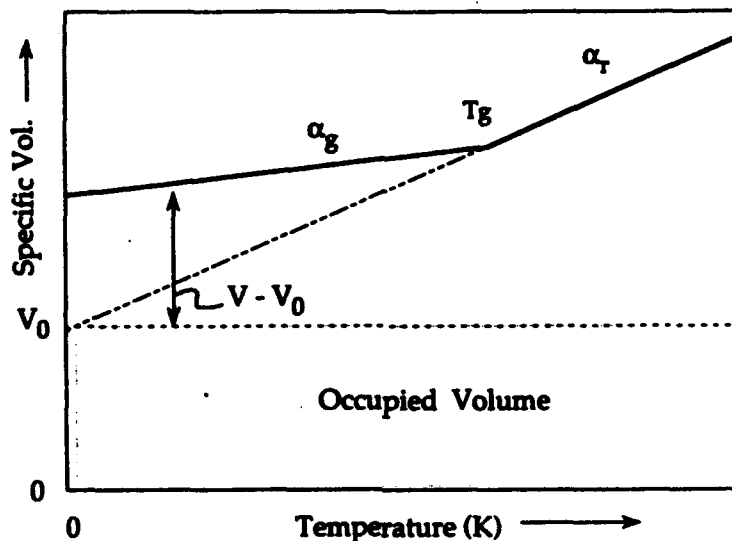
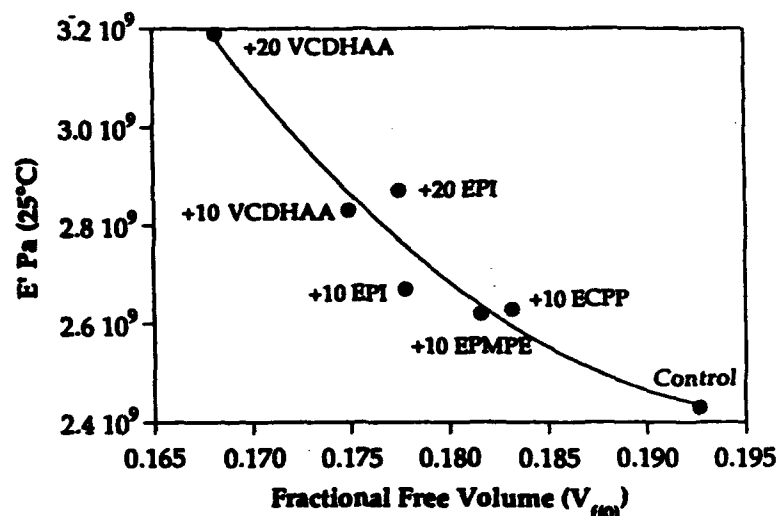


Fig.21 A simple schematic illustration of "free volume"

The specific volume (V) was obtained from density measurements, and its temperature dependence determined by thermomechanical analysis (TMA). The occupied volume (V_0) was determined by two methods - the epoxy and polyimide cases were slightly different as explained below. In the epoxy case, V_0 was calculated by extrapolation of the rubbery polymer expansion curve down to zero Kelvin. Note that this model leads to a free volume temperature term which depends on temperature even below the glass transition temperature - this is at variance with the Simha-Boyer model of free volume, but is consistent with the expansion volume concept of Bondi and Hildebrand and Bondi (16), and related models. The different interpretations of free volume are discussed particularly well by Haward (17).

The dependence of the modulus on the calculated free volume is illustrated in Figure 22. Clearly, as the free volume decreases the modulus increases, consistent with a picture involving hindered short-range motion of the polymer segments. Later, we will separate out the various contributions to the free volume decrease (molecular interactions and T_g depression both have a contribution to the free volume decrease)

Fig.22 The relationship between modulus and fractional free volume for the epoxy systems



An alternative way of looking at the phenomenon is to examine the effect of the additives on the beta relaxation. Figure 23 shows that the area under the tangent delta curve correlates well with the increase in modulus. This interpretation is discussed in more detail elsewhere (9,12), especially in terms of the spectrum of relaxation times, but we consider the change in the beta relaxation to be a consequence of the reduction in free volume, rather than vice versa.

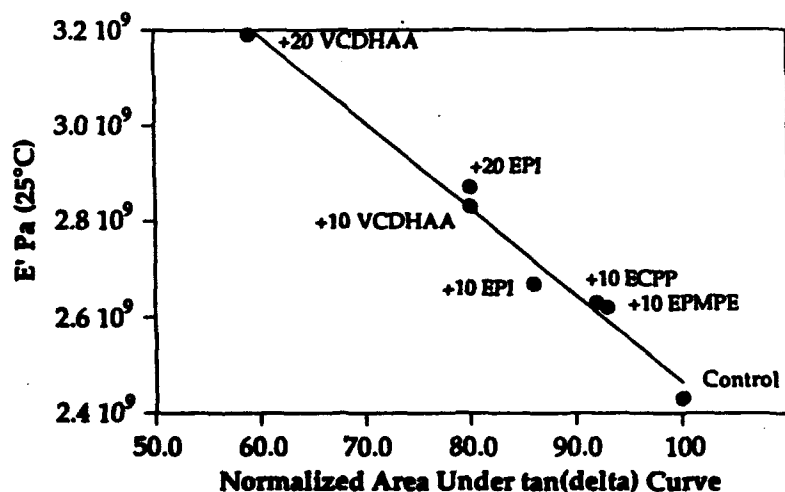


Fig.23 Storage modulus as a function of normalized area under the tangent delta curve of the beta relaxation

In the polyimide case, data for the expansion coefficient of the rubbery polymer is difficult to obtain (and in fact it is not clear what the concept of T_g really means in polyimides), and so V_0 was calculated from the sum of atomic contributions using the data of Sugden (18), as was done by Maeda and Paul (2). Note, also, that it was not possible to use this atomistic approach in the epoxy case, because for some additives

(particularly VCDHAA) the final composition of the modified crosslinked network was not known with sufficient precision. Tables 3 and 4 show the free volume calculations and modulus values for the PI-2540 polyimide and the Matrimid polyimide, and demonstrate that the polyimide/additive data can be explained by the same free volume as used for the epoxy system.

Table 3 Free volume and modulus for polyimide PI-2540

Sample	Specific Volume (cc/g)	Occupied Volume (cc/g)	Free Volume (cc/g)	% Free Volume	Modulus (GPa)
PI-2540	0.7026	0.5726	0.1300	18.50	3.40
+ 8.4% Fluorene	0.7047	0.6079	0.0968	13.74	3.62
+ 4.4% 9-Fluorenone	0.7052	0.5968	0.1084	15.37	3.82
+ 19.6% 2-Acetamidofluorene	0.7057	0.6219	0.0838	11.87	4.48
+ 2.8% 9-Hydroxyfluorene	0.7085	0.5949	0.1116	15.80	3.56
+ 18.5% Trichlorofluorene	0.6933	0.5981	0.0952	13.73	3.63
+ 24.8% EPPHAA	0.7180	0.6262	0.0918	12.79	4.38

Table 4 Free volume and modulus for Matrimid polyimide

Sample	Specific Volume (cc/g)	Occupied Volume (cc/g)	Free Volume (cc/g)	% Free Volume	Modulus (GPa)
Matrimid 5218	0.7990	0.6661	0.1330	16.64	3.06
+ 13.1% Fluorene	0.7991	0.6830	0.1161	14.53	3.23
+ 15.4% 9-Fluorenone	0.7910	0.6762	0.1148	14.51	3.55
+ 14.8% 2-Acetamidofluorene	0.7938	0.6787	0.1151	14.50	4.23
+ 13.1% 9-Hydroxyfluorene	0.7922	0.6760	0.1162	14.67	3.72
+ 15.9% Trichlorofluorene	0.7690	0.6604	0.1086	14.12	3.90
+ 19.1% EPPHAA	0.7882	0.6790	0.1092	13.85	4.34

Work is continuing on the modelling for the polyimide system. Since the additives do not modify the chemical state of the polyimide, it should be possible to relate the antiplasticizing action to a specific molecular characteristic of the additive (after separation of the T_g effect, see below)

One consistent effect of the additives, in both the polyimide and epoxy systems, is a reduction in T_g . In itself, this will have the effect of decreasing the free volume, and hence increasing the modulus, since the network can relax further on cooling. This is illustrated schematically in Figure 24. Given the detailed volumetric behavior of the polymer from TMA analysis, it should therefore be possible to separate out the " T_g contribution" to the modulus increase. The relative contributions of T_g reduction and molecular interactions are shown in Table 5, for the epoxy system. The T_g contribution is highest for VCDHAA because of the large T_g depression it causes, as a result of it incompletely reacting with the network (9). Additives such as EPI react fully with the network and so cause less of a T_g reduction. The molecular interaction term generally follows the polarity of the additive, although if longer chain additives

were used, it would also reflect the flexibility of the molecule (9). Note that if the T_g reduction term becomes sufficiently large (i.e. T_g approaches the test temperature), then the antiplasticizing effect will change into a plasticizing effect (see earlier figures on tensile curves at elevated temperatures)

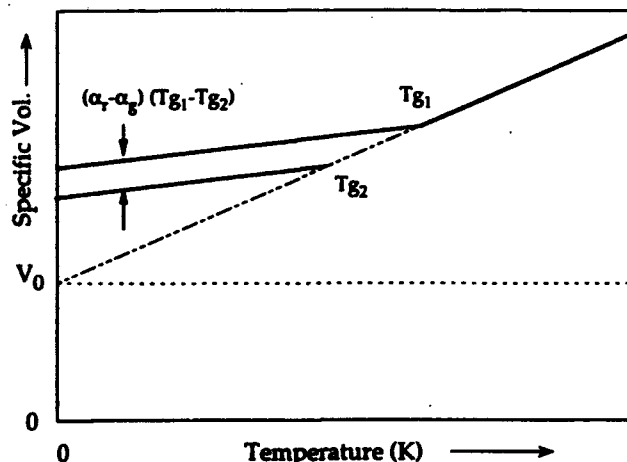


Fig.24 The reduction in free volume caused by a reduction in T_g

Table 5 The relative contributions of T_g reduction and molecular interactions to the modulus increase of the epoxy system

Sample	% Increase in Modulus	T_g Effect	Interaction Effect
+10 VCDHAA	16.5	4.4	12.1
+20 VCDHAA	31.5	10.8	20.6
+10 EPI	10.1	2.3	7.8
+20 EPI	18.2	6.9	11.3
+10 ECPP	8.5	3.9	4.6
+10 EPMPE	8.0	2.9	5.1

Before considering the origin of the yielding phenomenon, some other supporting evidence for this free volume interpretation should be mentioned. In collaboration with Dr.W.T.K.Stevenson, of Wichita State University, we examined the positron annihilation (PA) characteristics of the modified epoxy. PA is a means of probing the free volume using a positron source - the positrons will combine with the electrons in the specimen and a photon is emitted. Briefly, both the free volume and the hole size was shown by the PA technique to be decreased in the presence of the additive VCDHAA (19). A free volume decrease is also the origin of the physical aging phenomenon in glassy polymers (17), and so it is of interest whether the use of these additives can reduce physical aging by eliminating

the available free volume. A specimen of VCDHAA was sent to Dr.T.C.Ward of Virginia Tech, who is now exploring this hypothesis.

The occurrence of a yielding phenomenon (Fig.4) along with a modulus increase is surprising. We attribute this behavior also to free volume changes. Again in a simplified model, the free volume changes associated with strain can be equated to the free volume changes which accompany a temperature increase. Figure 5 shows that tensile strain results in an appreciable increase in volume for the epoxy system (i.e. Poisson's ratio < 0.5). TMA data provide the dependence of volume on temperature. These two sets of data may therefore be combined to introduce the concept of a "fictive temperature", i.e the temperature at which an unstrained polymer would have the same free volume as the strained polymer at room temperature (20). Such a plot is shown in Figure 25. The volume increase is greater for the VCDHAA-containing specimen (Fig.5), and its expansion coefficient is lower, and so the fictive temperature rises rapidly with strain for the VCDHAA-containing specimen. The arrows in Figure 25 mark the unstrained T_g , and indicate that the volume dilation on straining should cause yielding in the VCDHAA-containing specimen at less than five percent strain, as is shown in Figure 4. For the control, a strain of greater than eight percent is required for the fictive temperature to approach T_g , and fracture may intervene before this strain is reached, resulting in Brittle failure.

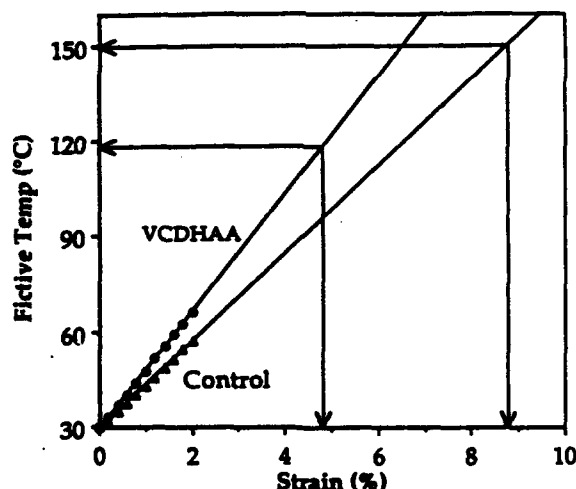


Fig.25 Fictive temperature vs. strain for epoxy systems

This model also predicts that the strain at yield should decrease with increasing temperature, since less free volume dilation is then required to attain T_g . Figures 7 and 8 show that this is indeed the case. Figure 26 illustrates the generality of this phenomenon for VCDHAA-containing specimens at a variety of temperatures. At high values of $(T_g - T)$, i.e. low test temperatures, the strain at yield (defined here, arbitrarily, as the strain at which the slope of the stress strain curve is zero) increases. The yielding phenomenon is therefore entirely consistent with a free volume interpretation of polymer properties. This explains why the yielding phenomenon is not associated with an increase in fracture energy.

A fracture energy test (compact tension specimen) involves a localization of the stress (and strain), and so the specimen is unable to take advantage of the bulk volume dilation which it experiences during a tensile test. While these materials can therefore be called "ductile" (provided the term is defined as the occurrence of yielding in the tensile curve), they should not be called "tough". This relatively subtle use of words has led to considerable misunderstanding among users. The additives increase the modulus, and usually the strength, but what effect they have on "toughness" will depend on the nature of the test for this ill-defined property.

B.7 Conclusions

1. The behavior of "epoxy fortifiers" can be explained on a quantitative basis using the concept of antiplasticization.
2. Monoepoxy additives can increase the modulus and strength of epoxy systems without as great a decrease in T_g as found with unreactive additives.
3. The yielding phenomenon in epoxy systems results from volume dilation during the tensile test. The yielding is not associated with an increase in fracture energy if compact tension specimens are used.
4. Other properties which are modified include water uptake, and expansion coefficient, both of which are relevant to adhesive applications.
5. Polyimides can be antiplasticized in a similar fashion, leading to an appreciable decrease in the rate of water uptake and increase in modulus. The phenomenon can again be treated on a quantitative basis using the concept of free volume.
6. The chosen additives do not react with linear polyimides, and so are examples of "external plasticizers". The monoepoxy additives in epoxy systems are examples of "internal antiplasticizers".
7. The monoepoxy additives show synergistic behavior when used with rubber toughening agents.
8. The modified epoxy system yields modest improvements in adhesive joint modulus and strength, but the magnitude of the change depends on the geometry of the joint. The improvement is greatest for low temperature-cured systems.
9. The reduced rate of water uptake by the modified polymers can lead to an improved retention of properties for adhesive joints in wet environments.
10. These additives may be used to generate modulus gradients at interfaces, which can improve the properties of adhesive joints and composites.

This research is continuing, on an unfunded basis, at least until the second student finishes his thesis (spring 1993). This will lead to further advances in understanding the polyimide additives. For additional details, please contact me personally.

Anders Carl

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11. E. Shockey, "Antiplasticization of Polyimides", Ph.D. Thesis, in preparation
12. Two further manuscripts (J. Polym. Sci., Polym. Phys. Edn. and Polym. Eng. and Sci., are in preparation. The polyimide reserach is continuing and will probably result in another publication

Participating Scientific Personnel

The PI (A.Garton) has been supported for three summer months on this project

Two Ph.D. students (Ed Shockey and Gautam Haldankar) have been supported full-time on this project

Unfunded collaborators include:

Paul McLean, National Research Council of Canada

William T.K.Stevenson, Wichita State University

Ken Reifsnider, VPI and graduate student

T.C.Ward, VPI and graduate student

The principal Army contacts have been R.Reeber, S.Wentworth, and W.Zukas, but a presentation was also made to Fort Belvoir personnel